

GROUP (V) AND (VI) TRANSITION METAL CARBIDES AS NEW CATALYSTS FOR THE REFORMING OF METHANE TO SYNTHESIS GAS

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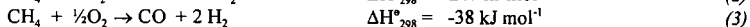
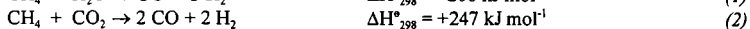
ABSTRACT

High surface area group V and VI transition metal carbides, synthesised by temperature programmed reduction of the metal oxides with methane/hydrogen, have been tested as catalysts for the dry reforming of methane with carbon dioxide and partial oxidation of methane with air. Mo₂C and WC were stable and highly active catalysts for these reactions at elevated pressure, while they deactivated at ambient pressure. The product distribution obtained was close to that predicted by the thermodynamic equilibrium, except that no carbon formation was observed on the catalyst surface. The carbides of niobium and tantalum deactivated, even in the dry reforming reaction at elevated pressure, due to their greater tendency towards oxidation.

INTRODUCTION

Synthesis gas (carbon monoxide and hydrogen) is an extremely important intermediate in the production of many chemicals, for example Fischer-Tropsch synthesis of hydrocarbons (e.g. in the Shell middle distillate process or at SASOL) and alcohols [1-3], ammonia synthesis (Fe catalysts) [4], methanol synthesis (Cu/ZnO/Al₂O₃) [5,6], and hydroformylation (homogeneous Rh catalyst) [7], and is also used in the reduction of iron ore. Of these many products, methanol, and higher alcohols, are often discussed as environmentally friendly fuel alternatives [8], while the development of hydrogen for use as an alternative fuel or in fuel cells is currently receiving much attention [9].

At present, synthesis gas is produced in great quantities from methane, mainly by the highly endothermic steam reforming process (1), and to a lesser extent by endothermic dry reforming with carbon dioxide (2); an alternative route is *via* the exothermic partial oxidation reaction (3).



Currently, nickel catalysts are employed industrially for both the steam reforming and dry reforming reactions [10], while partial oxidation is carried out autothermally [11]. However, since nickel also catalyses the carbon deposition reactions, methane decomposition and CO disproportionation (Boudouard reaction), an excess of oxidants is needed in order to prevent catalyst deactivation and blockages in the reactor tubes; this results in the production of synthesis gas with product ratios that are not optimal for further conversion downstream [10,12]. Alternative catalysts are the supported noble metals [13-18], or sulphur passivated nickel [19], both of which have been shown to exhibit kinetic resistance to carbon formation at or near stoichiometric reactant ratios; however, their application has been limited by the unfavourable economics and scarcity of the former, and the low activity of the latter.

In the past two decades, it has been shown that some transition metal carbides and nitrides, particularly those of group VI, possess catalytic properties similar to the noble metals [20-22]. Since the group VI transition metals are abundant and relatively cheap, it has been suggested that they can replace the scarce and expensive noble metals for a number of catalytic applications. Initial problems centred on the synthesis of high specific surface area (S_g) materials suitable for use as catalysts. However, following the publication of a number of methods for the synthesis of metal carbides/nitrides with $S_g \leq 220 \text{ m}^2 \text{ g}^{-1}$ [23-25], it was shown that these materials were active for a number of catalytic reactions, including alkane isomerization, ammonia synthesis, and Fischer-Tropsch synthesis, to name only a few [26].

In this paper we present the results of methane dry reforming and partial oxidation over the group V and VI transition metal carbides. We have found that the high surface area carbides of molybdenum and tungsten, under stoichiometric reactant feeds and elevated pressure, are

stable and highly active catalysts for these reactions; no carbon formation was observed over the carbide surface during the reactions.

EXPERIMENTAL

Catalyst Synthesis and Characterisation

The high surface area metal carbide materials were prepared using the temperature programmed reduction method pioneered by Boudart and co-workers [23]: briefly the low surface area metal oxide powder was heated in flowing 20% CH_4/H_2 mixture from room temperature to 1000-1223K, depending on the oxide (discussed later), at 1 K min^{-1} . Normally the catalysts were prepared *in situ* and tested immediately. The post-synthesis high surface area carbides are readily and exothermically oxidised by air at room temperature and, therefore, passivation in flowing 1% O_2/N_2 for 10 hours at room temperature was carried out before exposure to the atmosphere and characterization. Crystalline components of the materials were identified by X-ray diffraction (XRD) using a Philips PW1710 diffractometer with $\text{Cu-K}\alpha$ radiation.

Catalyst Testing

The apparatus used in this work was a modified version of the commercial Labcon microreactor described previously [27]. The reactor was built using 1/8" and 1/16" o.d. 316 stainless steel tubing and 316 stainless steel Swagelok fittings throughout. The catalyst sample was placed between two quartz wool plugs in the centre of a 4 mm i.d. silica tube and inserted into a vertical Severn Science tube furnace, heated to the required reaction temperature and controlled from a Eurotherm 905 temperature controller. For safety reasons, in experiments carried out at elevated pressures the silica tube was placed inside a steel tube. Inlet gas flow rates were controlled using Brooks 5850TR mass flow controllers, and the exit gas stream from the reactor passed through a Tescom two stage back-pressure regulator to allow elevated pressure experiments to be carried out. All the pipework was heated to prevent condensation of the products.

Product analysis was carried out using a Hewlett-Packard 5890II gas chromatograph, fitted with both a thermal conductivity detector, and a methanator/flame ionization detector. Separation of the products was achieved using a 3m Porapak Q packed column, with argon carrier gas. In all cases stoichiometric gas mixtures were used and carbon balances were better than 97%.

RESULTS AND DISCUSSION

Synthesis and Characterisation

Synthesis of the metal carbides was carried out using temperature programmed reduction with CH_4/H_2 , as mentioned above, and it was noticed, by monitoring the effluent gas by real-time mass spectrometry, that the final temperature needed for complete formation of the carbide varied from 1023K for molybdenum carbide to 1223K for tantalum carbide; this is due to the relative reducibility of the oxides.

Some of the characterising data obtained for the metal oxides and metal carbides studied are presented in Table 1. The metal carbide phase formed was determined by XRD of passivated samples; the structures were identified by comparison with the literature [28]. No metal oxide could be seen in any of the diffraction patterns, showing that the passivation method only results in the oxidation of the surface of the carbide samples, while the bulk remains unaffected. N_2 BET of passivated metal carbide samples confirmed that high surface area materials had been synthesised.

Methane Dry Reforming with Carbon Dioxide

The results obtained for the dry reforming of methane with carbon dioxide over bulk NbC_x , TaC_x , $\beta\text{-Mo}_2\text{C}$ and $\alpha\text{-WC}$, as well as over bulk SiC , are presented in Table 2. The silicon carbide (Norton Materials UK) used here had a low surface area ($\approx 1 \text{ m}^2 \text{ g}^{-1}$), and had very low catalytic activity for the dry reforming reaction. Indeed, at 1223K, the methane and carbon dioxide conversions were only 13.3% and 3.4% respectively, while at 1373K the conversions were much higher, due to the important role of autothermal processes. Thus, it can be concluded that the autothermal contribution is minor at or below 1223K, i.e. in the temperature range used for the catalytic study of the carbides.

The results obtained for Mo_2C and WC , presented in Table 2, are extremely similar to those expected from thermodynamics, demonstrating that these materials are efficient catalysts for methane dry reforming; in contrast, NbC_x and TaC_x gave relatively low conversions and yields, except when the temperature was increased to 1373 K. This indicates that the carbides of niobium and tantalum are formed, but that they are only stable at very high temperatures (and probably higher pressures). Indeed, Figure 1 shows that Mo_2C is the most stable of the carbides tested, while NbC_x and TaC_x deactivated rapidly at 1223K; NbC_x was stabilised to some extent at 1373K, but the high H_2/CO ratio given in Table 2 indicated that carbon formation was occurring at this high temperature, probably *via* autothermal reactions. The stability of WC was found to be

extremely similar to that of Mo_2C under the conditions employed here (not shown), with no deactivation observed for > 72 h on stream at 8 bar and 1223 K. Further, Figure 1 shows that elevated pressures are required to stabilise the catalysts. Powder XRD of post-catalytic $\beta\text{-Mo}_2\text{C}$ samples demonstrated that the deactivated sample contained a large amount of MoO_3 , which has only a very low activity for methane dry reforming, while the stabilised catalyst had only peaks due to the starting carbide. The reason for the deactivation of the NbC_x and TaC_x samples is that these materials are less stable than the carbides of Mo and W, as borne out by the higher temperature needed to synthesise the carbide; this means that, under the equilibrium conditions existing during the reaction, oxidation of NbC_x or TaC_x proceeds more readily than recarbideation.

Since carbon formation is a well known problem in methane dry reforming, post-catalytic samples of $\beta\text{-Mo}_2\text{C}$ and $\alpha\text{-WC}$ were studied by high resolution electron microscopy (not shown). No carbon deposits were observed on the catalyst surface, even under our stoichiometric reactant feeds; this compares favourably with the results published previously for commercial nickel catalysts [29].

Methane Partial Oxidation with Air

Table 3 shows the results obtained for the partial oxidation of methane with air, over $\beta\text{-Mo}_2\text{C}$ and $\alpha\text{-WC}$. Oxygen conversion was essentially 100% for all the experiments. As before, when the oxidation reactions were carried out at ambient pressure the catalyst deactivated by forming MO_2 , although the deactivation occurred much more quickly in the presence of air than was the case with carbon dioxide, meaning that an initial activity could not be obtained. However, when the partial oxidation was carried out at elevated pressure the catalyst activity was stabilised, and no deactivation was observed for the duration of the experiments (> 72 h), as shown in Figure 2 for $\beta\text{-Mo}_2\text{C}$. Post-catalytic XRD of the samples showed that no phase changes had occurred, and that no MO_2 or MO_3 had been formed during the reaction. This is particularly important in the case of molybdenum, since the formation of MoO_3 at these high temperatures would lead to loss of catalyst by vaporisation, or movement of the catalyst along the reactor tube. HRTEM of the post-catalytic samples indicated that no carbon deposition had occurred on the catalyst surface during the reaction.

The effect of temperature and pressure on the product distribution was determined using a $\beta\text{-Mo}_2\text{C}$ catalyst, at temperatures between 1073 K and 1223 K and at pressures varying from 3 to 12 bar; the results obtained are presented in Figures 3a and b. As the temperature was increased or the pressure decreased, the conversion of methane and selectivity to carbon monoxide increased; these trends can be predicted from thermodynamic calculations, and demonstrates that the carbides are efficient catalysts for this reaction.

CONCLUSIONS

We have found that high surface area molybdenum and tungsten carbides are stable catalysts for the stoichiometric carbon free reforming of methane with carbon dioxide and air at elevated pressure. These materials are much cheaper than the platinum group metals, e.g. MoO_3 is 2000 times cheaper than platinum [30], so they may be useful alternatives to conventional industrial catalysts for synthesis gas production. Methane dry reforming with niobium and tantalum carbides showed that these materials are less stable, although niobium carbide was stabilised when very high temperatures were used.

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TABLES

Table 1. Some characteristics of the metal carbides synthesised by CH₄ TPR.

Precursor	Carbide phase	Structure	CH ₄ TPR synthesis	
			Final T / K	S _g / m ² g ⁻¹
MoO ₃	β-Mo ₂ C	h.c.p.	1023	91
WO ₃	α-WC	h.c.p.	1153	39
Nb ₂ O ₅	NbC _x	f.c.c.	1173	62
Ta ₂ O ₅	TaC _x	f.c.c.	1223	54

x = 0.70-0.99 [NbC_x] and [TaC_x].

Table 2. Results for the dry reforming of methane over the group V and VI transition metal carbides (GHSV = 2.87 × 10³ h⁻¹, CH₄/CO₂ = 1).

Catalyst	T / K	P / bar	C[CH ₄] / %	C[CO ₂] / %	Y[CO] / %	H ₂ /CO
SiC	1223	8.0	13.3	3.4	8.1	-
	1373	8.0	76.3	75.2	75.7	0.90
NbC _x	1223	8.0	67.6	77.3	72.4	0.82
	1373	8.0	83.7	96.3	90.0	1.33
TaC _x	1223 [†]	8.0	54.7	61.5	58.1	0.67
β-Mo ₂ C	1123	1.0 [†]	92.4	92.5	92.5	0.93
	1223	1.0 [†]	98.8	95.9	95.9	0.92
	1123	8.3	62.5	75.9	69.5	0.78
	1223	8.3	83.3	89.5	86.5	0.88
α-WC	1123	1.0 [†]	92.0	93.1	92.6	0.94
	1123	8.3	62.7	75.4	68.6	0.79

[†] catalyst deactivates; * initial result could not be obtained.

Table 3. Results for the partial oxidation of methane over molybdenum and tungsten carbide catalysts (T = 1173 K, GHSV = 5.25 × 10³ h⁻¹, CH₄/air = 2/5).

Catalyst	P / bar	C[CH ₄] / %	S[CO] / %	S[CO ₂] / %	H ₂ /CO
β-Mo ₂ C	8.7	88	92	8	2.02
α-WC	8.7	89	90	10	2.05

FIGURES

Figure 1. Stabilities of the transition metal carbides for methane dry reforming ($\text{CH}_4:\text{CO}_2 = 1:1$).

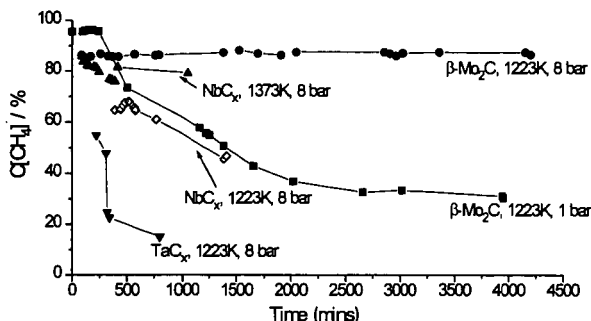


Figure 2. Lifetime study of $\beta\text{-Mo}_2\text{C}$ for the methane partial oxidation reaction at 8.7 bar ($T = 1173\text{ K}$, $\text{GHSV} = 5.25 \times 10^3\text{ h}^{-1}$, $\text{CH}_4/\text{air} = 2/5$).

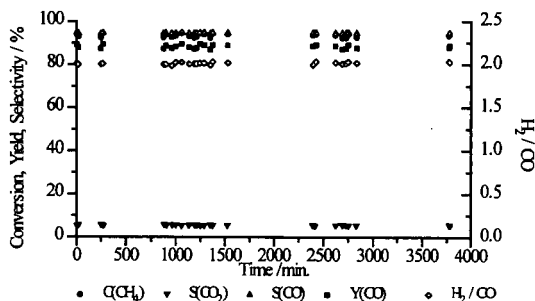


Figure 3a. Effect of temperature on the partial oxidation of methane over $\beta\text{-Mo}_2\text{C}$ (8.7 bar, $\text{GHSV} = 5.25 \times 10^3\text{ h}^{-1}$, $\text{CH}_4/\text{air} = 2/5$).

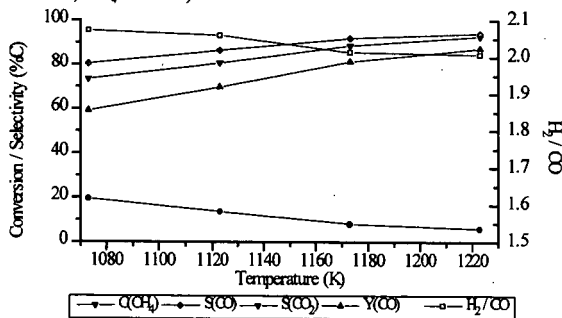


Figure 3b. Effect of pressure on the partial oxidation of methane over $\beta\text{-Mo}_2\text{C}$ (1173 K, $\text{GHSV} = 5.25 \times 10^3\text{ h}^{-1}$, $\text{CH}_4/\text{air} = 2/5$).

